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Anisotropy of mobility ratio between electron and hole along different orientations in $\text{ReGe}_x\text{Si}_{1.75-x}$ thermoelectric single crystals

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It was recently found that $\text{ReSi}_{1.75}$ based semiconductor single crystals can be of either p or n type with a fixed composition, just depending on their different crystal orientations. To investigate the mechanism of this interesting phenomenon, we grow $\text{ReGe}_x\text{Si}_{1.75-x}$ ($x=0.02$ and 0.04) single crystals with a floating zone method with radiation heating. The Seebeck coefficient and electric resistivity of these samples are measured along $[100]$ and $[001]$, respectively. The conduction mechanism is of p type along $[100]$ and of n type along $[001]$, like binary $\text{ReSi}_{1.75}$, in the temperature range 50 to 800 °C. The mobility ratio between electron and hole is calculated from the Seebeck coefficient data and it is highly anisotropic along two different orientations (about 0.4 to 0.6 along $[100]$ while 4 to 5 along $[001]$ direction), giving rise to the orientation-dependent conduction sign reversal phenomenon observed in $\text{ReSi}_{1.75}$.

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$\text{ReSi}_{1.75}$, a silicide formed with the refractory transition metal rhenium, is of interest first owing to its application as a narrow gap semiconductor in infrared detectors.¹⁻⁵ It also has the potential to be used as thermoelectric materials, which have attracted a renewed and considerable interest in the past decade.^{6,7} Recently, in addition to their excellent thermoelectric properties, we observed a reversal of conduction sign in terms of the crystal orientation for binary and doped (e.g., $\text{Mo}_x\text{Re}_{1-x}\text{Si}_{1.75+x}$) $\text{ReSi}_{1.75}$ single crystals.⁸ That is, the mechanism of the conduction in these semiconductors is surprisingly of p type along one direction while it is of n type along the other direction, which is very rare for semiconductors to the best of our knowledge. This experimental evidence suggests the existence of a “two faces” semiconductor family in nature, whose members can be of either p type or n type with a fixed composition, just depending on their different crystal orientations. As for thermoelectric materials this means some semiconductors that usually show bad thermoelectric properties as polycrystals might have the chance to be nice thermoelectric candidates in some special orientation when they are grown as single crystals. Hence, the investigation of the mechanism of this interesting phenomenon becomes one of the important objects of our research, as well as the investigation of the ways to increase the thermoelectric performance of this silicide.

$\text{ReSi}_{1.75}$ has a monoclinic structure with an ordered arrangement of Si vacancies in the underlying C11_b structure, whose unit cell is shown in Fig. 1. The Seebeck coefficient, which is defined as (dV/dT) , is an important value for evaluating a material's ability to make conversion between heat and electricity (V and T , respectively, denote the voltage and the temperature). As for semiconductors, it is generally believed that the measured sign of the Seebeck coefficient exhibits a material's conduction nature. That is, the positive Seebeck coefficient suggests holes are dominant in the measured material while the negative one means electrons are dominant. For binary $\text{ReSi}_{1.75}$ single crystals, the measured Seebeck coefficients are negative along the $[001]$ direction of

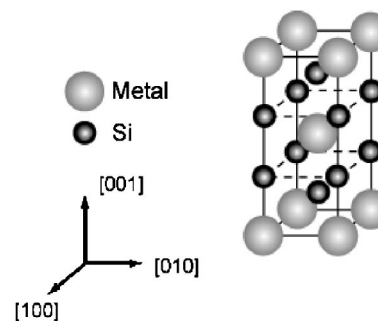


FIG. 1. Unit cell of C11_b structure. As for $\text{ReSi}_{1.75}$, some Si atoms are absent from their due positions. These Si vacancies are ordered arranged in the underlying C11_b structure.

the C11_b structure while they are positive along $[100]$, in the temperature range 100 to 800 °C. Hall coefficient measurements also give the same results for the conduction type.⁸ Since $\text{ReSi}_{1.75}$ is a narrow gap semiconductor and this phenomenon occurs especially in a temperature range far higher than room temperature, both electrons and holes should play important roles in the conduction process. Hence, we focus on investigating the carrier mobility ratio between electrons and holes (μ_e/μ_h) for this silicide. We consider that this ratio, which represents the comparative sensitivity of holes' and electrons' drifting velocity to the imposed electric field, dominates the conduction process when the densities of electrons and holes are comparable.

In this report, we calculate the mobility ratio of Ge-doped $\text{ReSi}_{1.75}$ together with binary $\text{ReSi}_{1.75}$ since Ge has the same number of valence electrons as Si. We suppose any member of these $\text{ReGe}_x\text{Si}_{1.75-x}$ single crystals, with the different Ge content x , will have a similar Seebeck coefficient changing tendency, giving rise to the close mobility ratio calculation results. We have grown single-crystal samples of $\text{ReGe}_x\text{Si}_{1.75-x}$ ($x=0.02$ and 0.04) by a floating zone method with radiation heating. A bar-type specimen ($3 \times 3 \times 10$ mm for $[100]$ and $3 \times 3 \times 6$ mm for $[001]$) was cut from the high-

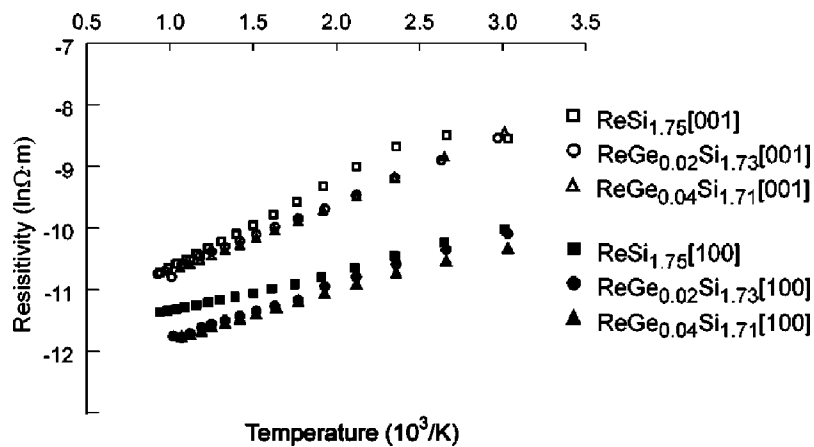


FIG. 2. Temperature dependence of electric resistivity for $\text{ReGe}_x\text{Si}_{1.75-x}$ single crystals along [100] and [001]. Data of $\text{ReSi}_{1.75}$ [100] and [001] are quoted from Ref. 8. In [001] direction, the calculated energy gap is 0.25, 0.19, and 0.20 eV, respectively, with the increase of Ge content. In [100], the gap is 0.11, 0.15, and 0.13 eV, respectively.

quality single crystal with its specimen axis precisely parallel to either [100] or [001]. Electric conductivity and Seebeck coefficient were measured simultaneously with the thermoelectric measuring system ZEM-2 manufactured by ULVAC, Japan.

X-ray diffraction and transmission electron microscopy observation results indicate that the crystal structure and the microstructure (containing four domains, see Ref. 8) of $\text{ReGe}_x\text{Si}_{1.75-x}$ are almost the same as those for binary $\text{ReSi}_{1.75}$, except its lattice constants are slightly larger than those for the binary counterpart, probably due to the larger size of Ge atoms than Si atoms.

Changes in electric resistivity of $\text{ReGe}_x\text{Si}_{1.75-x}$ single crystals along [100] and [001] are shown in Fig. 2. The slopes of $\ln \rho$ versus $1/T$ curves are nearly constant, which confirms the intrinsic conduction is dominant in all Ge-doped samples. Thus, the band gap values of different samples can be calculated from these slopes. These are 0.25, 0.19, and 0.20 eV along [001] and 0.11, 0.15, and 0.13 eV along [100], respectively, for alloys with the Ge content x of 0, 0.02 and 0.04. The results are in the range that has been reported before for binary $\text{ReSi}_{1.75}$.⁹⁻¹³

Values of Seebeck coefficients of $\text{ReGe}_x\text{Si}_{1.75-x}$ single crystals along [100] and [001] are presented together in Fig. 3. The conduction here is of p type along [100] direction while it is of n type along [001], as in the case of binary $\text{ReSi}_{1.75}$. For further discussion, we emphasize two points as listed below:

1. The conduction mechanism in all samples is intrinsic, since the energy gap is small and the measurements were made in a comparatively high temperature range. Hence both holes and electrons participate in the conduction behavior and we suppose the densities of holes and electrons are equal.

2. In such a temperature range, the phonon scattering dominates the scattering process, which gives $\tau \propto E^{-1/2}$ at a set temperature, where τ is the relaxation time for the scattering.

According to the expression given in Chap. 6.2 of Ref. 14, we describe the Seebeck coefficient in pure electron conduction case as

$$S_e = \frac{k}{e} \left[\frac{E_F - 2F_1/F_0}{kT} \right], \quad (1)$$

where the function F_n is defined as $F_n = \int_0^\infty |E - E_{v(c)}|^n f_0 dE$ and f_0 is the Fermi-Dirac distribution function. Other parameters have their usual meaning and point 2 is adopted to deduce Eq. (1). It should be noted that Boltzmann distribution is unsuitable here since the band gap is too small to fully satisfy the request ($|E_{c(v)} - E_F| > 2kT$) for the material to be nondegenerate, especially at temperatures higher than room temperature.

Similarly, the Seebeck coefficient in pure hole conduction case can be expressed as

$$S_h = \frac{k}{e} \left[\frac{-E_F + 2F_1/F_0}{kT} \right], \quad (2)$$

When both holes and electrons participate in conduction behavior, the general expression of Seebeck coefficient is

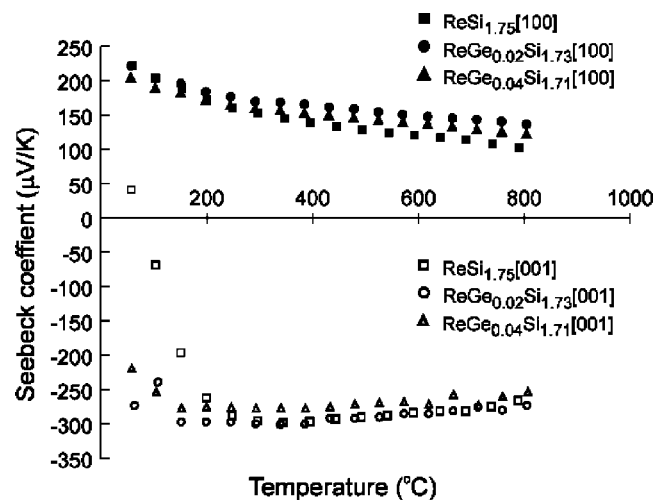


FIG. 3. Seebeck coefficients of $\text{ReGe}_x\text{Si}_{1.75-x}$ single crystals along [100] and [001]. It should be noted that it is positive along [100] while negative along [001]. Data of $\text{ReSi}_{1.75}$ along [100] and [001] are quoted from Ref. 8.

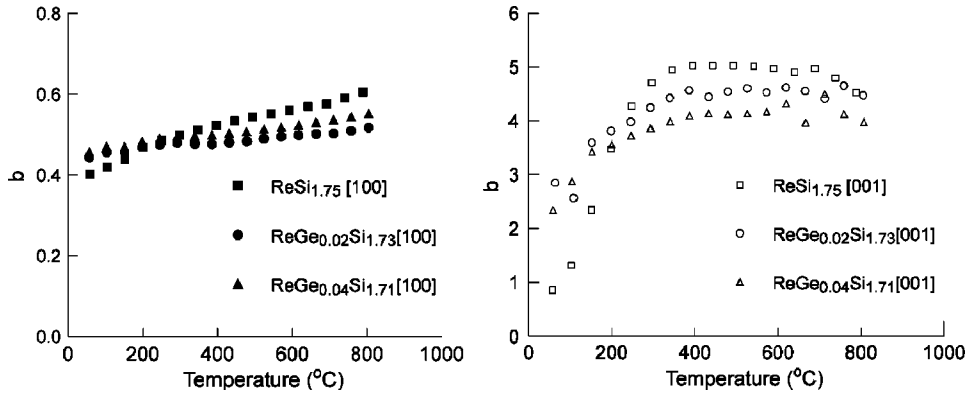


FIG. 4. Carrier mobility ratios between electrons and holes for $\text{ReGe}_x\text{Si}_{1.75-x}$ along [100] and [001], respectively. Mobility ratios deduced from Ref. 16 are 28.2 along [001] and 0.68 along [100]. Results of binary $\text{ReSi}_{1.75}$ along [100] and [001] are calculated from the data listed in Ref. 8.

$$S = \frac{n\mu_e S_e + p\mu_h S_h}{n\mu_e + p\mu_h}, \quad (3)$$

where n , p , μ_e , and μ_h are the electron density, hole density, electron mobility, and hole mobility, respectively. As having been assumed before, $n=p$ and supposing $E_f = -0.5E_g$ (the bottom of the conduction band is set as zero), we can plot the mobility ratios between electron and hole (μ_e/μ_h) along [100] and [001], respectively, in Fig. 4, as a function of temperature. The mobility ratio b between electron and hole is highly anisotropic for [001] and [100] orientations, giving rise to the clear reversal of the conduction sign. Moreover, the b value for binary $\text{ReSi}_{1.75}$ along [001] is larger than 1, which may result in the negative Hall coefficient for $\text{ReSi}_{1.75}$ along [001], as was observed before.⁸

The origin of such phenomenon may be explained by the band structure of $\text{ReSi}_{1.75}$. Up to now, both experimental¹⁰⁻¹³ and theoretical^{15,16} information about the carrier transport properties of $\text{ReSi}_{1.75}$ is limited. References 15 and 16 calculated its band structure with the LMTO and FLAPW method, respectively. It was reported that for $\text{ReSi}_{1.75}$ there are four conduction band edges at the S point (first Brillouin zone edge, $[110]_{\text{C11}_b}$ direction) and one valence band edge at Γ .^{15,16} The effective masses of electron and hole, which are deduced from the band calculation along main directions, are listed in Ref. 16. We calculated the mobility ratio b according to these data following

$$\frac{\mu_e}{\mu_h} = \frac{m_{hc}m_{hd}^{1.5}}{m_{ec}m_{ed}^{1.5}}, \quad (4)$$

where m_c is the conducting effective mass and m_d is the density-of-state effective mass. The former is

$$\frac{1}{3} \left(\frac{1}{m_a} + \frac{1}{m_b} + \frac{1}{m_c} \right)$$

and the latter is $6^{2/3} \times \sqrt[3]{m_a m_b m_c}$ for electrons in Si. The mobility ratio calculated from Eq. (4) is, respectively, 28.02 along [001] and 0.68 along [100]. The b values deduced from Ref. 16 in both directions are somewhat larger than

those from the Seebeck coefficient data. To be noted here is that the band structure calculations in Refs. 15 and 16 are based on the C11_b structure with a random distribution of Si vacancies in two Si positions with 75% occupancy¹⁰ while it is found that Si vacancies are actually arranged in $\text{ReSi}_{1.75}$ in an ordered manner,⁸ which may affect the band calculation results. Moreover, for $\text{ReSi}_{1.75}$, the b values deduced from the band calculation and from the Seebeck coefficient data are almost in agreement with each other along [100], while the mobility ratio calculated from the band calculation is much larger than the value deduced from the Seebeck coefficient data along [001] (see Fig. 4). This might be explained by the existence of high-density twin domains (with thickness 50–200 nm, see Ref. 8) along [001], which may have unneglectable effects on carrier behaviors.

In summary, we have calculated the mobility ratio between electron and hole for $\text{ReGe}_x\text{Si}_{1.75-x}$ ($x=0, 0.02, 0.04$) single crystals along [100] and [001], respectively. The ratios are highly anisotropic for [100] and [001] orientations, giving rise to the conduction sign reversal in $\text{ReSi}_{1.75}$ for these two orientations. This phenomenon may not be only the case for $\text{ReSi}_{1.75}$. Any semiconductor single crystal with such E - k curve as conduction or valence band, which is flat in some orientations while being widely dispersed in some other orientations near band edges, might have the potential to exhibit an orientation-dependent conduction sign reversal. As for thermoelectric materials, the polycrystalline materials made up from this kind of single crystal may show bad thermoelectric properties, since the property of the individual crystal grain inside can counteract each other when the grains are randomly arranged. However, they have the chance to be nice thermoelectric candidates, like $\text{ReSi}_{1.75}$ in some special orientations, when they are grown as single crystals.

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